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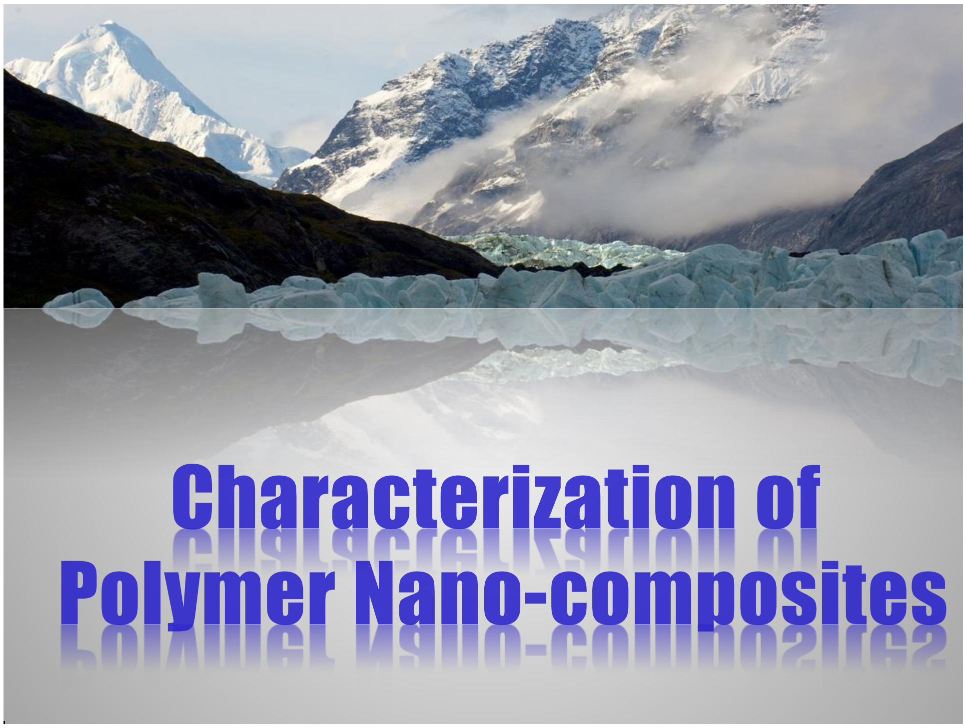

پلیمرها

۱
- استفاده بی سابقه در کامپوزیت ها

۲
- استفاده روز افزون در زمینه های بایو

۳
- توسعه فرمالیسیون جدید

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Nanotechnology Areas

Nanocomposites

Fire retardant plastics: Bayblend FR incorporating nanoparticle

Thin Layer and Surfaces

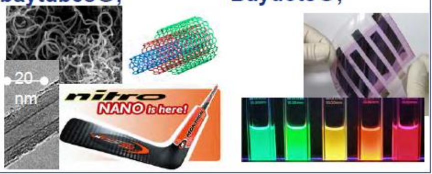
Surface Modification: Scratch Resistance, UV-Protection, Easy-to-Clean

Adhesives: Bonding Strength, Thermal Stability, Processing

Nanoparticle / - additives

Carbon nanotubes – baytubes®,

Quantendots – Baydots®,



Nanobiotechnology

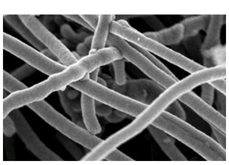
Liposomes, Diagnostics, Drug Delivery

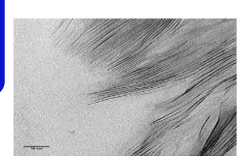
3

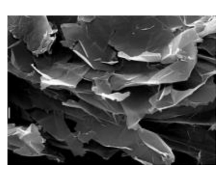
Why Nano-materials?

Small size

- **Strong**
- **High surface area**
- **Unique physical properties**


Carbon nanotubes


Nano-clay platelets in Epoxy resin


Graphite nanoplatelets

Have ability to reinforce polymers

-www.prlog.org www.materialsri.com, http://www.npl.co.uk
-www.physik.uni-augsburg.de www.xgsciences.com , www. cnx.org;
-C. Liu, Zhenning Yu, David Neff, Aruna Zhamu and Bor Z. Jang, 2010, *10* (12)

4

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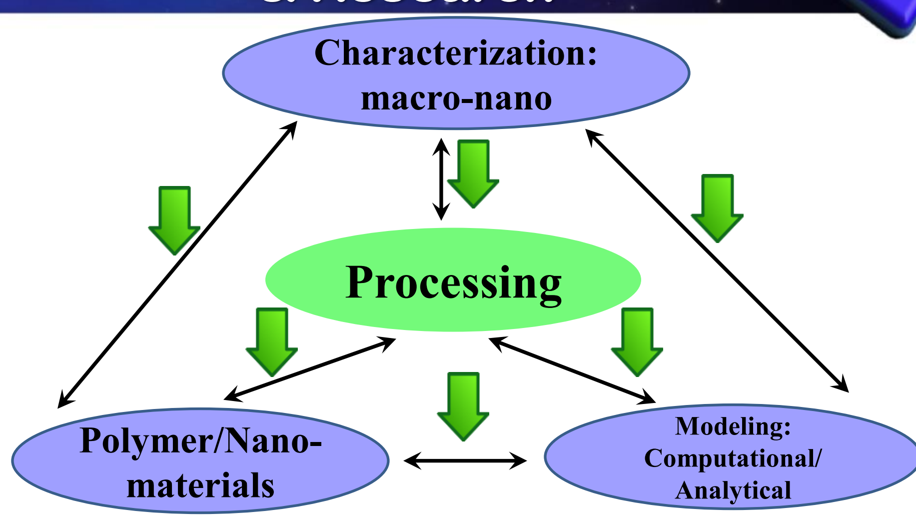
Big Challenges!

1. عدم شناخت از سیستم های موجود
2. عدم آگاهی از خروجی سیستم ها
3. تفسیر نتایج؟
4. ارتباط منطقی نتایج

Interrelationships & Research



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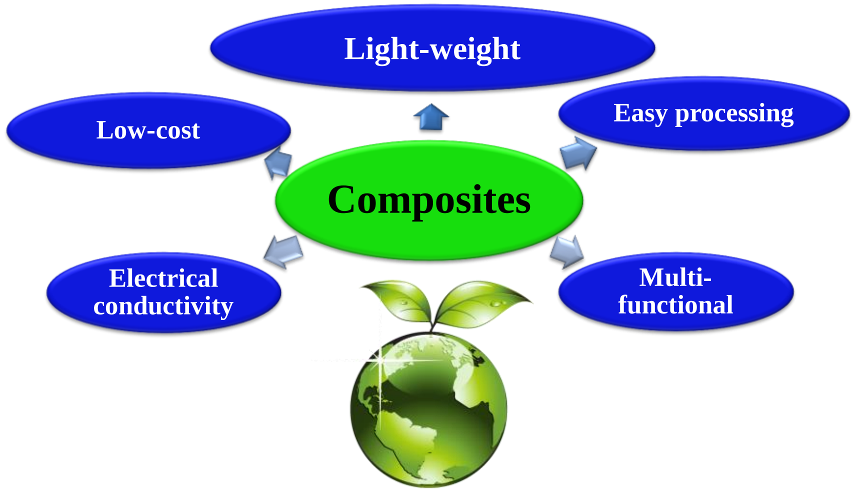
Why composites?



-http://www.universal-web-design.com
-E. T. Thostenson, C. Li and T.-W. Chou, *Composites Science and Technology* **2005**, *65*, 491-516

How to Beat Polymers?

What is Rheology ?

- **The science of <u>flow</u> and <u>deformation</u> of matter.**
- **Rheology: <u>the study of stress-deformation relationships.</u>**

What is a Rheometer?

An instrument that measures both **viscosity** and **viscoelasticity** of fluids, semi-solids and solids

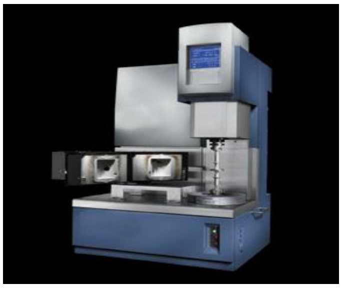
It provides following information about the material's:

1. **Viscosity** (which is the function of shear rate or stress, time & temperature dependence)
2. **Viscoelastic properties** (G', G", tan δ) with respect to time, temperature, frequency & stress/strain
3. **Transient response** (relaxation modulus, creep compliance, creep recovery)

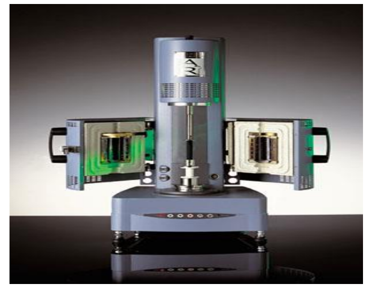
Types of Rheometers

- **Rotational** (Shear) Rheometers
  - ARES (Strain Control – SMT)
  - AR (Stress Control – CMT)
- **Solids** (Tensile/Bending) Rheometers
  - RSA (Strain Control – SMT)
  - DMA Q800 (Stress Control – CMT)

Rheometers



ARES SERIES
(SMT)



AR SERIES
(CMT)

Thermal Analysis of Materials

- **Polymers** (Thermoplastics, thermosets, Elastomers, Polymer blends, copolymers).
- **Foodstuffs** and **Pharmaceuticals**
- **Inorganic** (Minerals & Clays)
- **Ceramics**, **metals** and **Alloys**.
- **Petroleum** derived products (fuels, greases, Lubricating oils).

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ACRONYMS

- DSC: Differential Scanning Calorimtery
- TGA: Thermo Gravimetric Analyzer
- SDT: Simultaneous Differential Thermal Analyzer
- DMA: Dynamic Mechanical Analyzer
- TMA: Thermo Mechanical Analyzer

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Thermal Analysis of Materials Reveals

- **Low energy Transitions (β, γ, Coefficients): DMA**
- **Glass transitions (Tg): DSC, TMA, DMA**
- **Softening: TMA, DSC, DMA**
- **Melting: DSC, TMA, DMA**

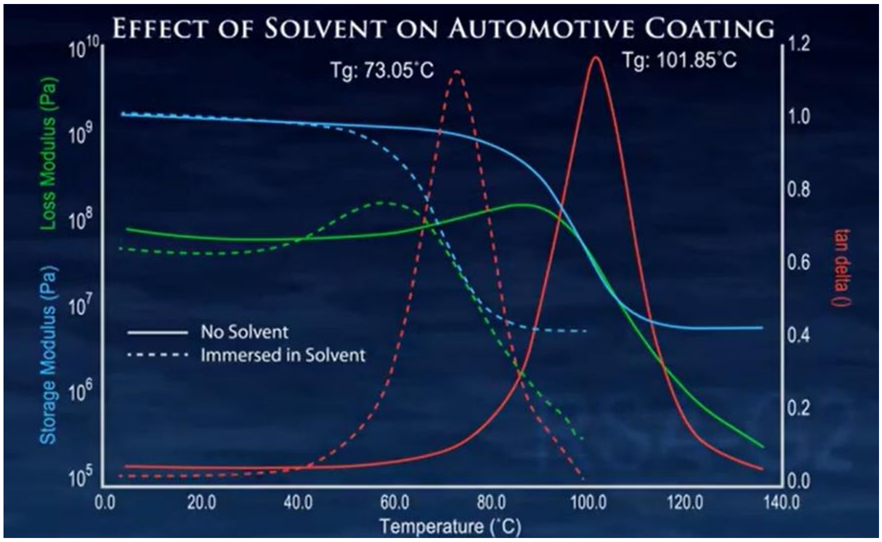
Thermal Analysis Measurements

- Heat flow and heat capacity: DSC, MDSC
- Weight change: TGA
- Dimension changes: TMA
- Modulus and damping: DMA

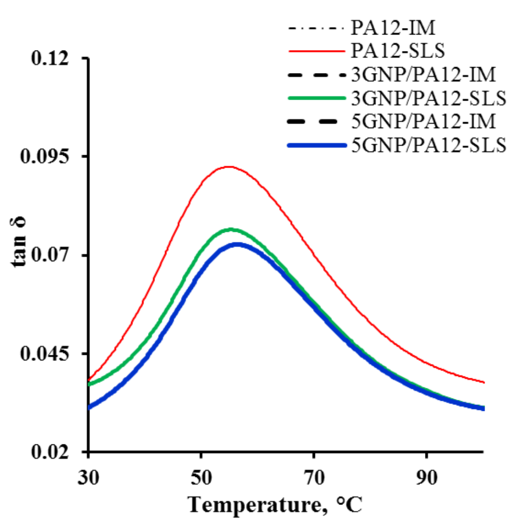
Thermal Analysis of Materials Reveals

- Re-ordering (Curing): DSC, TMA, DMA
- Thermal/Oxidative stability & weight change: TGA

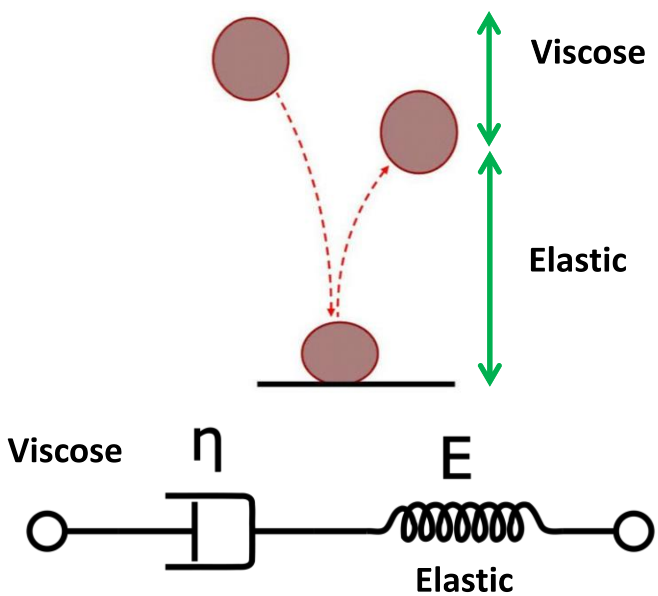
Another Easy Method?



Another Easy Method?



Elastic+ Viscoelastic Properties



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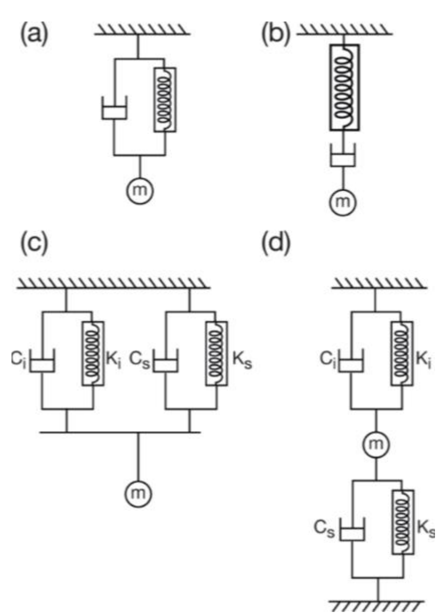
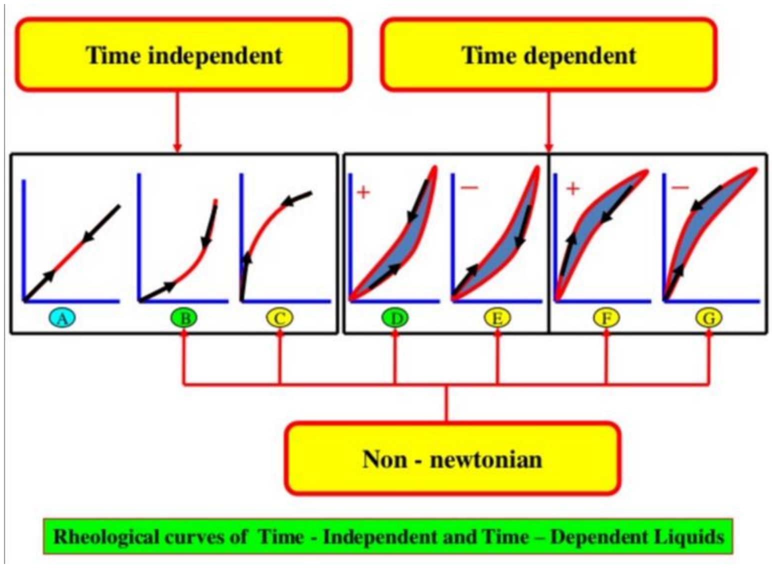
Elastic+ Viscoelastic Properties



Rheological Curves



Actual Example: Foams

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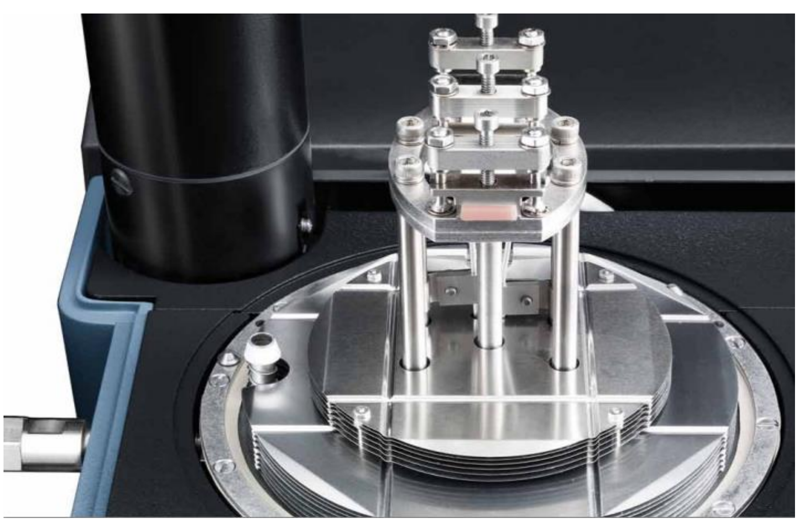
Dynamic Mechanical Analysis DMA)

Dynamic Mechanical Analysis (DMA)



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- DMA 1
- DMA 2
- DMA 3

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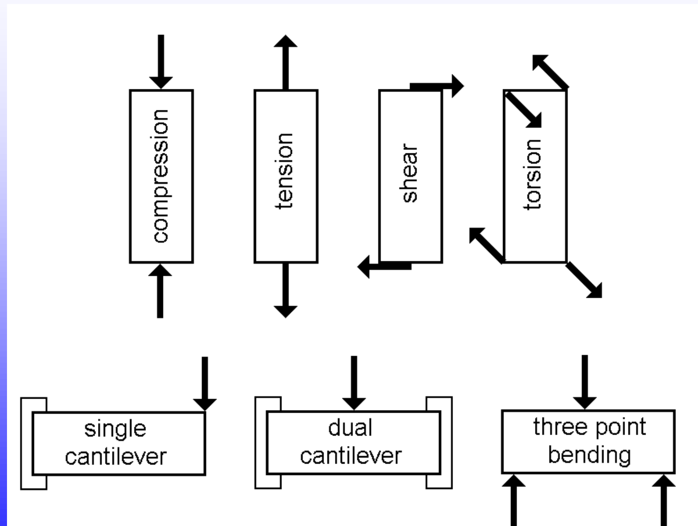
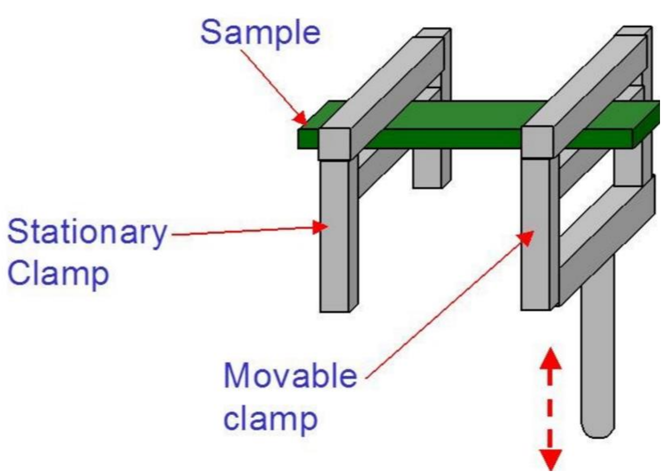
Dynamic mechanical analysis

- **Dynamic mechanical analysis** (**DMA**): **viscoelastic** behavior of polymers.
- A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the modulus.
- The temperature of the sample or the frequency of the stress are often varied, leading to variations in the modulus.
- This approach can be used to locate the **glass transition temperature** of the material.

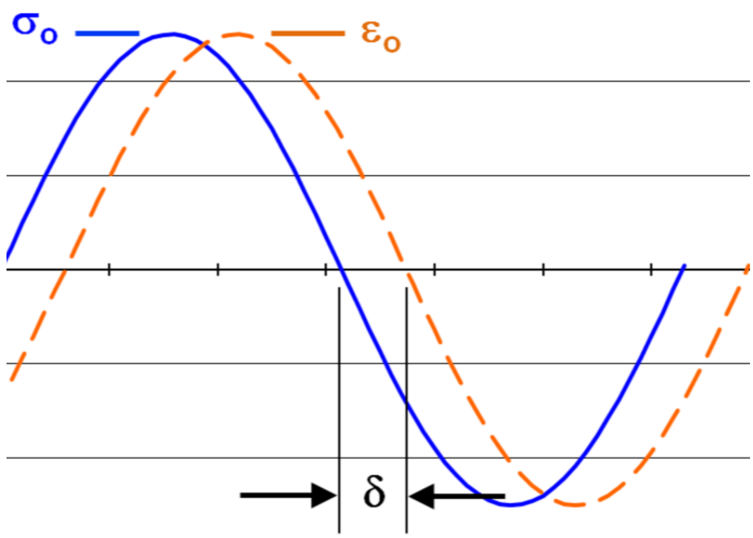
Test Configurations



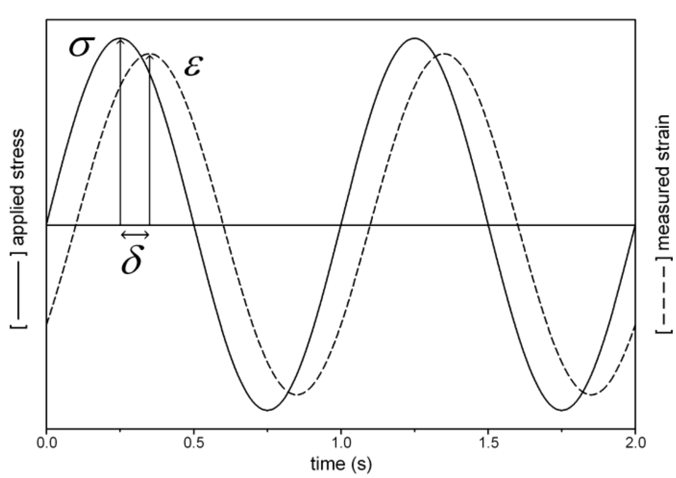
Test Configurations



Phase Lag: A Measure of Damping



Phase Lag: A Measure of Damping



DMA: E' and E"

- DMA: **stiffness** and **damping**, these are reported as **modulus** and **tan delta**.
- Modulus can be expresesed as;
- in-phase: the storage modulus **(E')** and
- out of phase: the loss modulus **(E")**

- **Storage modulus (E')** is a measure of elastic response of a material. It measures the stored energy.

- **Loss modulus (E")** is a measure of viscous response. It measures the energy dissipated as heat.

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DMA: E' and E"

Tan delta is the ratio of loss to the storage and is called damping.

$$\tan \delta = E''/E'$$

E" = storage modulus
E' = loss modulus

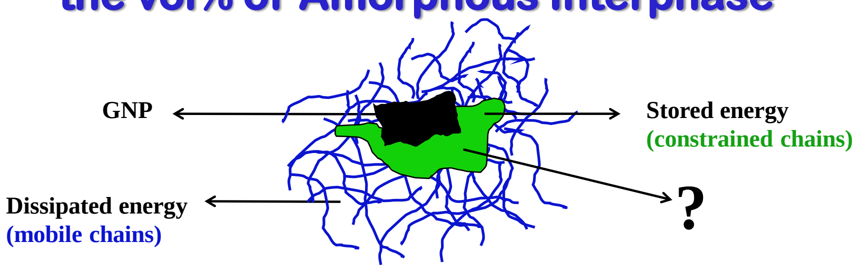
- Basically tan delta can be used to characterize the modulus of the material.
- Delta should range between 0° and 90° and as delta approaches 0° it also approaches a purely elastic behavior.
- As delta approached 90° the material approaches a purely viscous behavior.

Some part of the applied load is dissipated by the energy dissipation mechanisms (such as segmental motions) in the bulk of polymer , and other part of the load is stored in the material and will be release upon removal of the load (such as the elastic response of a spring!).

- **Increasing** Tan delta indicates that your material has more energy dissipation potential so the greater the Tan delta, the more dissipative your material is.
- **Decreasing** Tan delta means that your material acts more elastic now and by applying a load, it has more potential to store the load rather than dissipating it!

For example, in case of **nano-composites** (and filled polymers), increasing the nano-particle content diminishes the value of Tan delta as nano-particles impose restrictions against molecular motion of polymer chains (due to the adsorption of polymer chain on the surface of the particles) resulting in more elastic response of the material.

Experimental Determination of the vol% of Amorphous Interphase



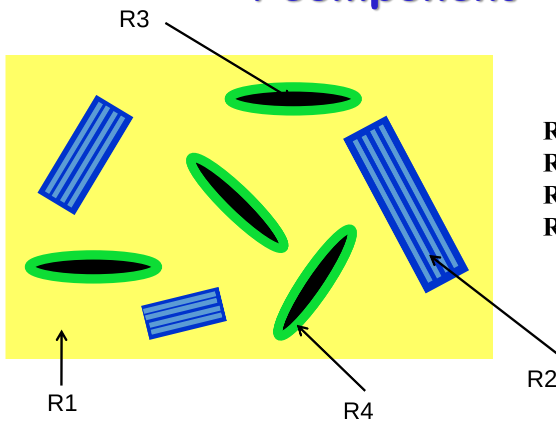
Approach: The ratio of the dissipated energy ➡ The fraction of amorphous mobile segments, hence[1,2]

$$C = 1 - \frac{W}{W_0}(1 - C_0) \qquad (1) \qquad\qquad W = \frac{\pi \tan\delta}{\pi \tan\delta + 1} \qquad (2)$$

where C is fraction of constrained chains, W and W_0 the energy loss ratios of the composite and neat polymer from DMA; C_0 the degree of crystallinity in pure polymer

[1] J. Kalfus and J. Jancar, *Polymer* **2007**, *48*, 3935-3937.
[2] Kojima Y, Usuki A, Kawasumi M, Okada A, et. al., Journal of Materials Research(USA). 1993;8:1185-1189.

Composite system 4-component



R1-Amorphous matrix
R2- Crystalline domain
R3-Fillers
R4-Interphase

- Addition of fillers has nucleating effect and generates small crystallites with tremendous surface area.
- Better dispersion of fillers pronounces this effect.

Constrained Fraction

- In liner viscoelastic regime, the relationship among E',E" and the energy loss fraction can be expressed as:

$$W = \frac{\pi E''}{\pi E'' + E'} = \frac{\pi . \tan\delta}{\pi . \tan\delta + 1}$$

- This energy loss is directly proportional to the fraction of amorphous matrix, α:

$$W \propto \alpha$$

$$\alpha + C = 1$$

- α=R1, C=R4+R2

- Establishing a reference equation using the concept for the pure polymer, we have:

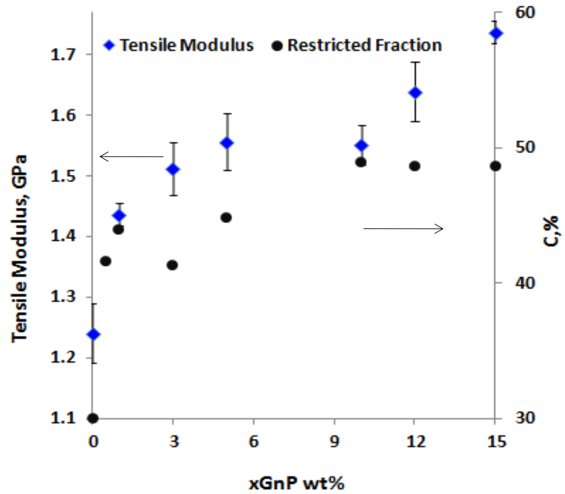
$$W_0 \propto \alpha_0$$

$$\alpha_0 + C_0 = 1$$

Constrained Fraction: Case Study

- Using the ratio of the loss energy values of both the systems, the constrained fraction of the matrix can be calculated:

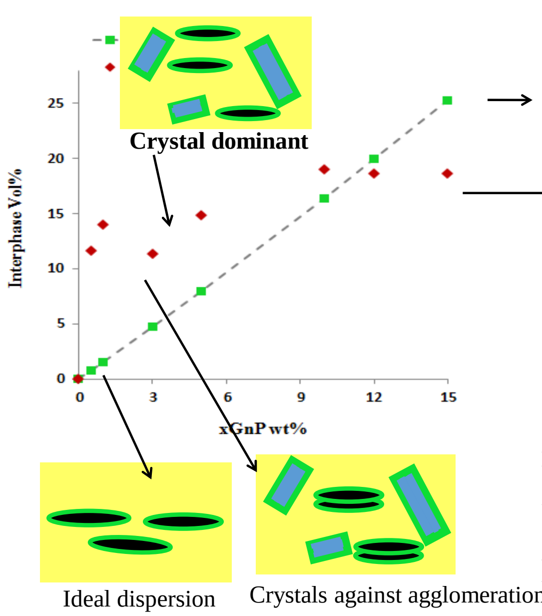
$$C = 1 - \frac{W}{W_0}(1 - C_0)$$

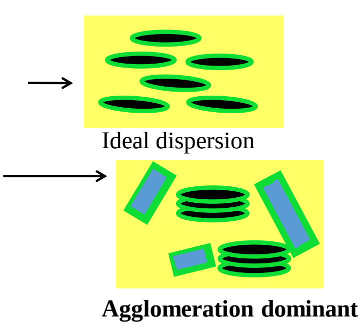


- Increase in C% for the content up to 1 wt%, and then drop in the amount of the constrained region before it grows again

- Initial remarkable shift in modulus and C% coincides

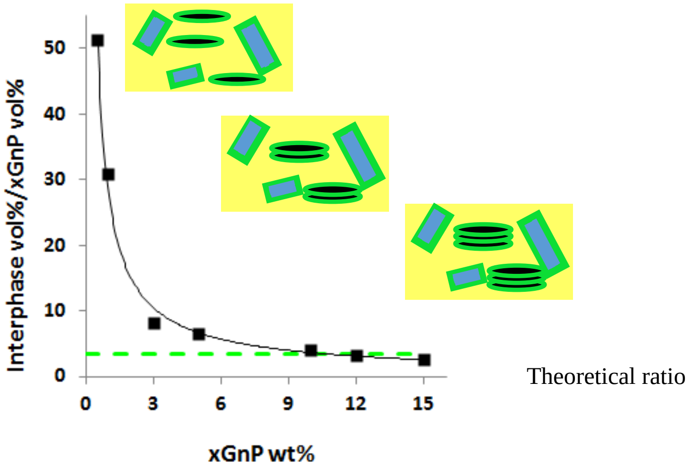
Amorphous Constrained Interphase v.s. Theoretical Interphase





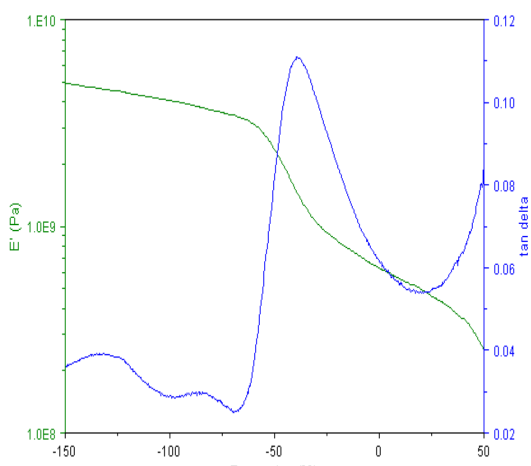
Crystallites contribute to formation of interphase, so the measured amount of interphase is greater than the theoretical amount up to the average loadings.

Interphase/filler Ratio
Agglomeration Degree



• The ratios lower than the theoretical values indicates presence of severe agglomeration.

• Using the actual amount of interphase and geometry of the fillers, the size of agglomerates can be estimated by defining their aspect ratio .



For example, the DMA curve of polycaprolactone measured at a mechanical vibration frequency of 1 Hz is shown below:

The drop in storage modulus (E') and peak in damping factor (tan delta) between -60 and -30°C is due to the glass transition (Tg) of the amorphous polymer in this semi-crystalline material. Above 50°C the sample begins to melt and flow, thus loosing all mechanical integrity. Below the Tg small peaks are evident in the tan delta curve at -80 and -130°C. These are the beta and gamma transtions in this polymer (the glass transition is known also as the alpha transition) and are caused by local motion of the polymer chains as opposed to large scale co-operative motion that accompanies the Tg. These small transitions are very difficult to observe by DSC but are often very important in determining the impact resistance of the polymer.

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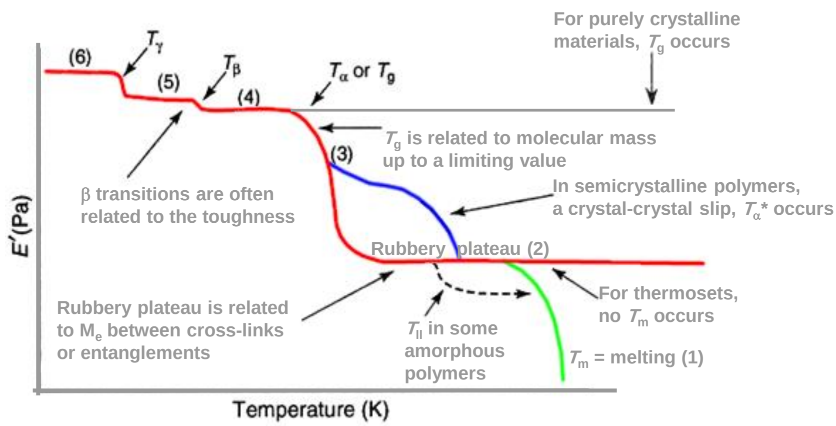
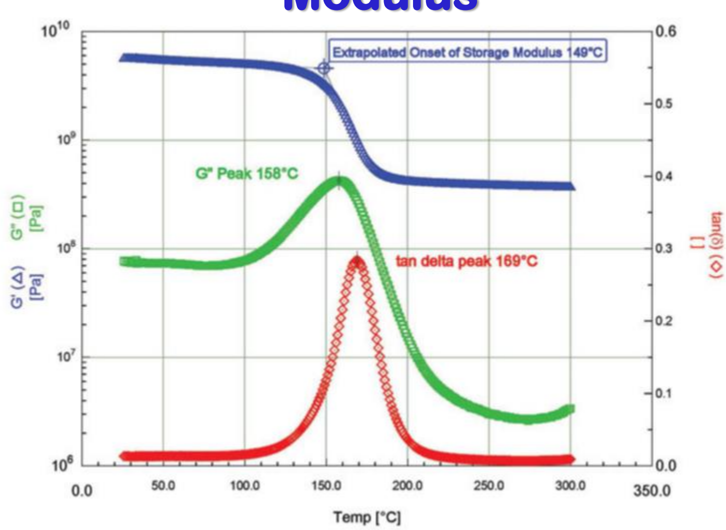
Typical Behaviour



Stress Relief: Decrease in Modulus



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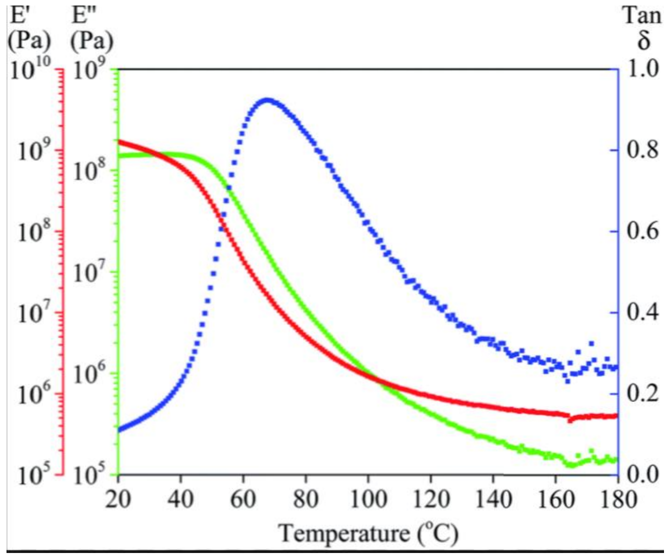
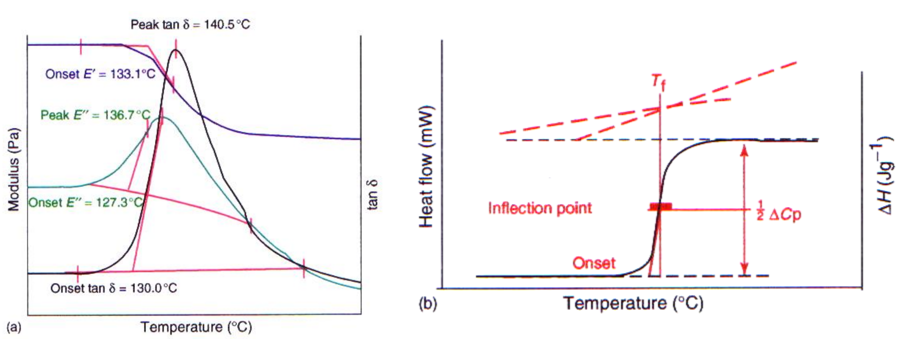
Stress Relief: Decrease in Modulus



Determination of Tg



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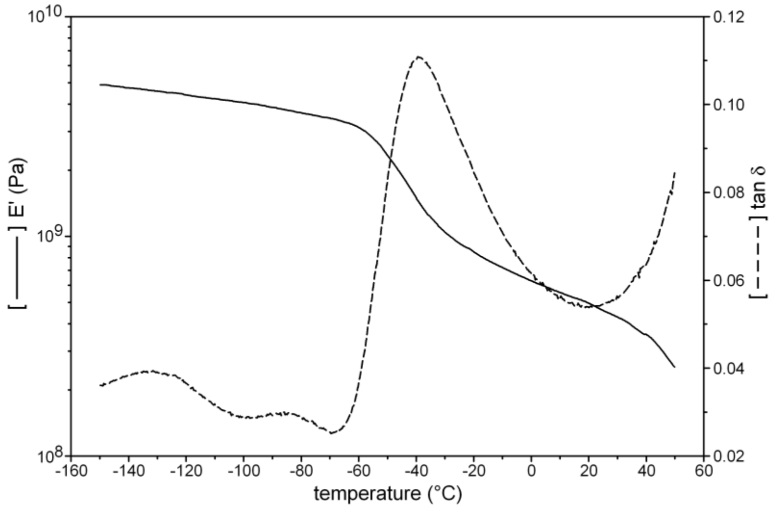
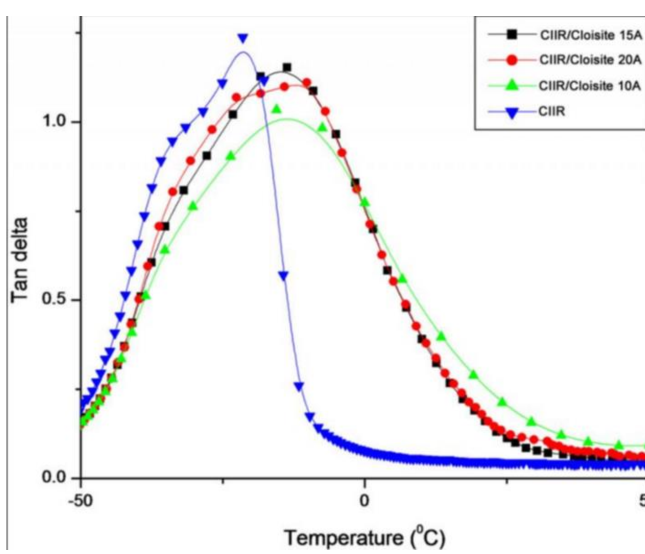
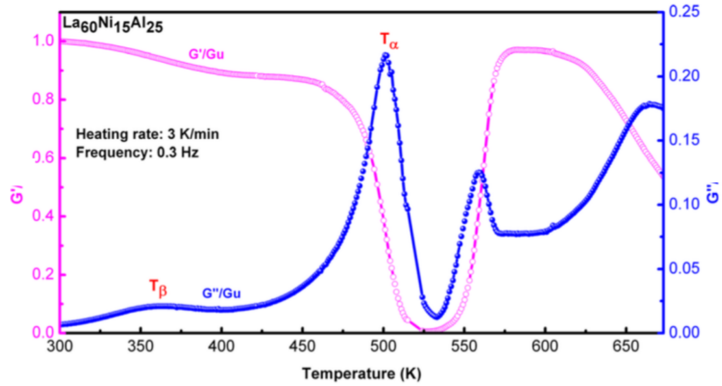
Polycaprolactone (PCL) Bio-polymer



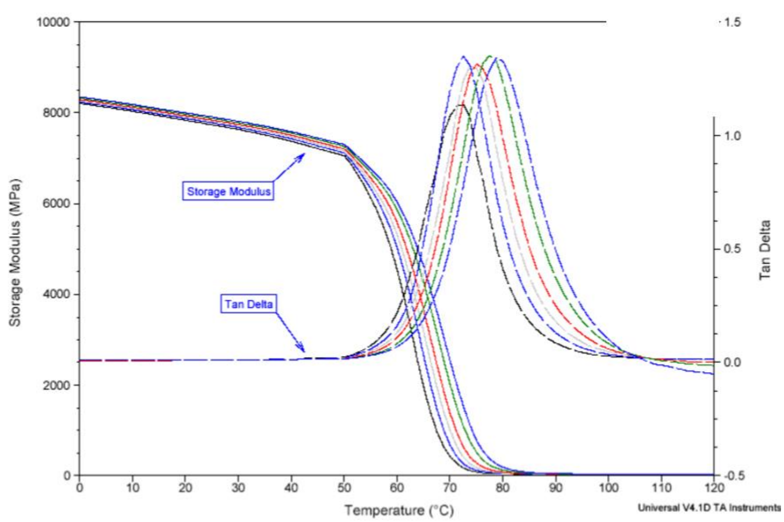
Tan δ



Loss, Storage Modulus and tan δ: Nylon



Loss, Storage Modulus and tan δ: Nano-composites



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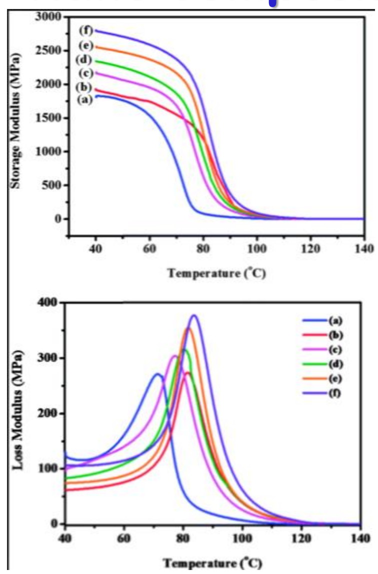
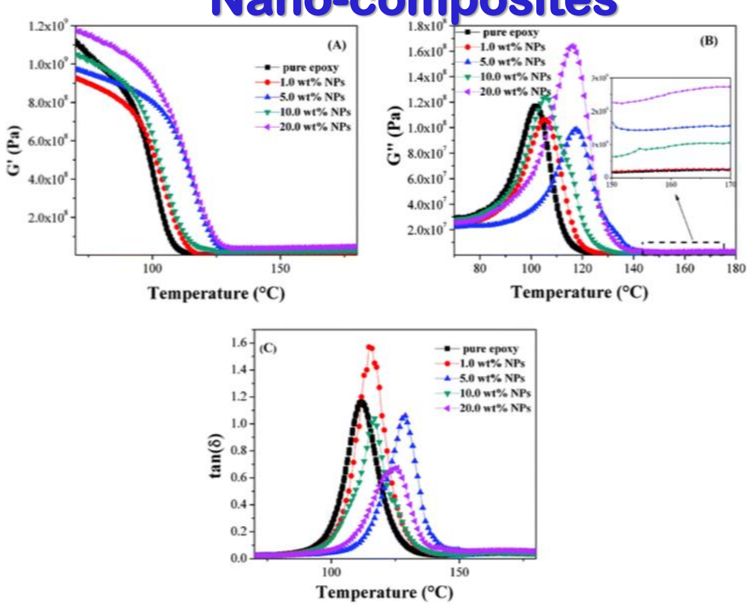
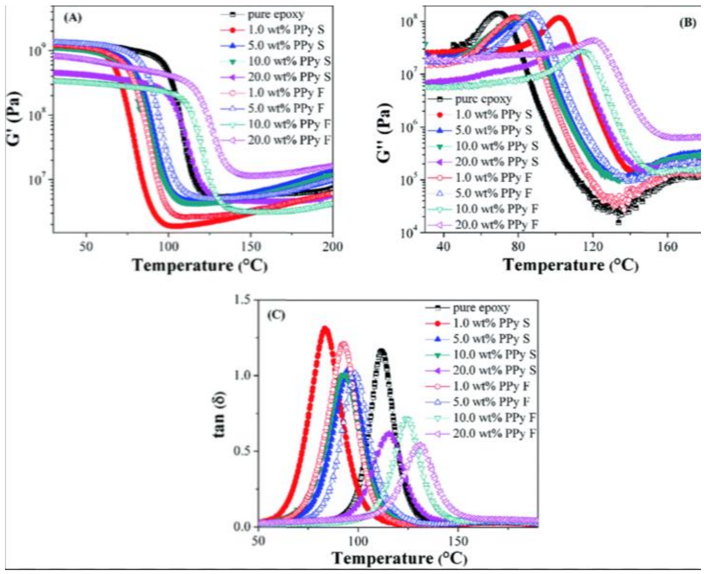
Loss, Storage Modulus and tan δ: Nano-composites



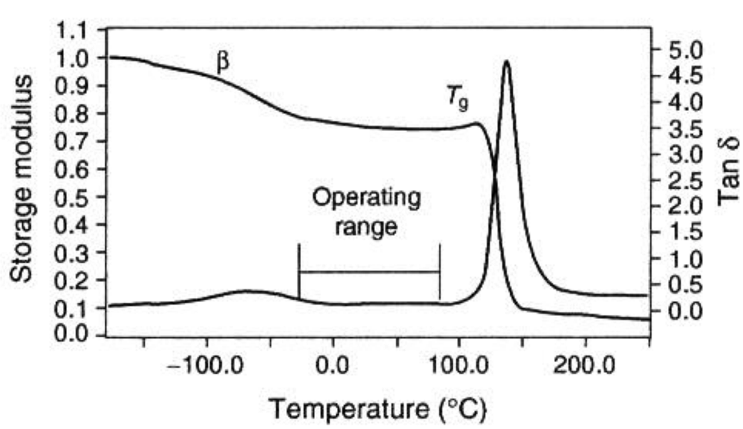
Loss, Storage Modulus and tan δ: Nano-composites



Loss, Storage Modulus and tan δ: Nano-composites



Operating Range



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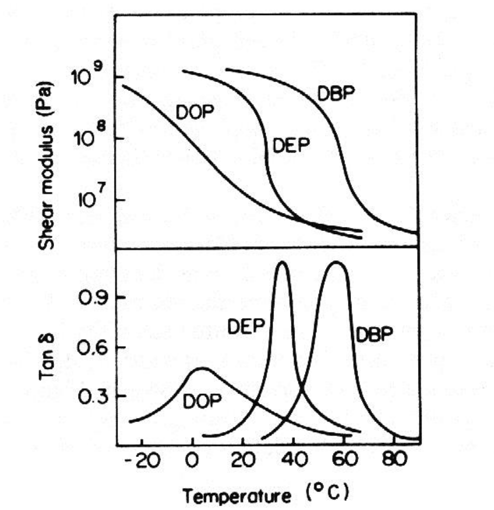
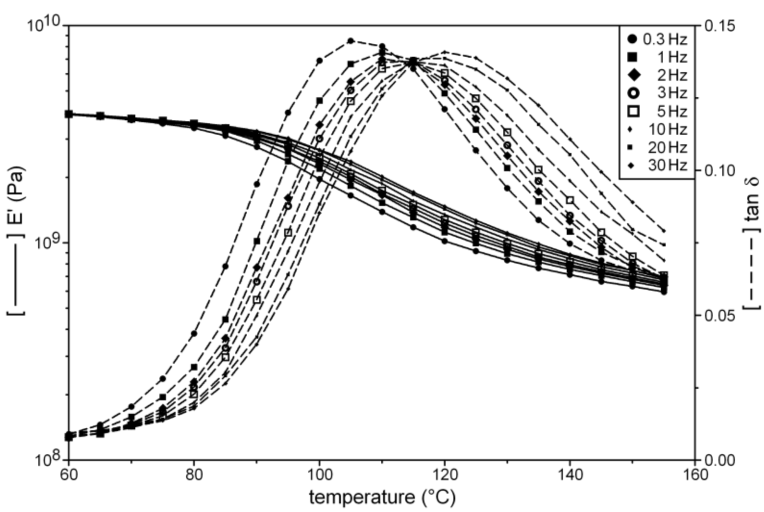
Effect of Plasticiser



Effect of Frequency



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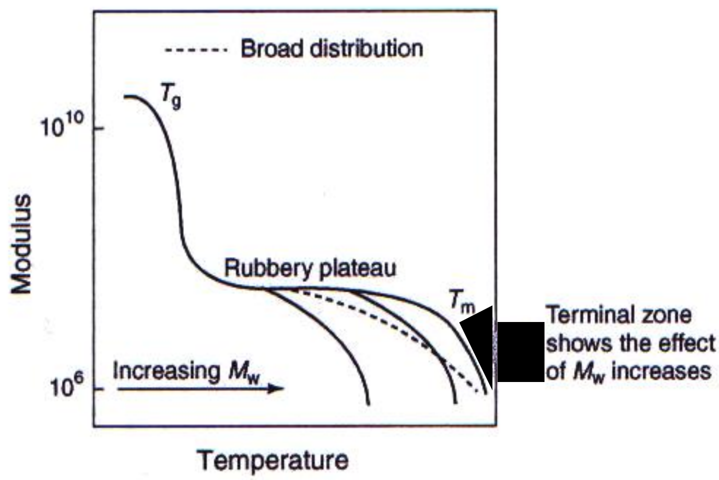
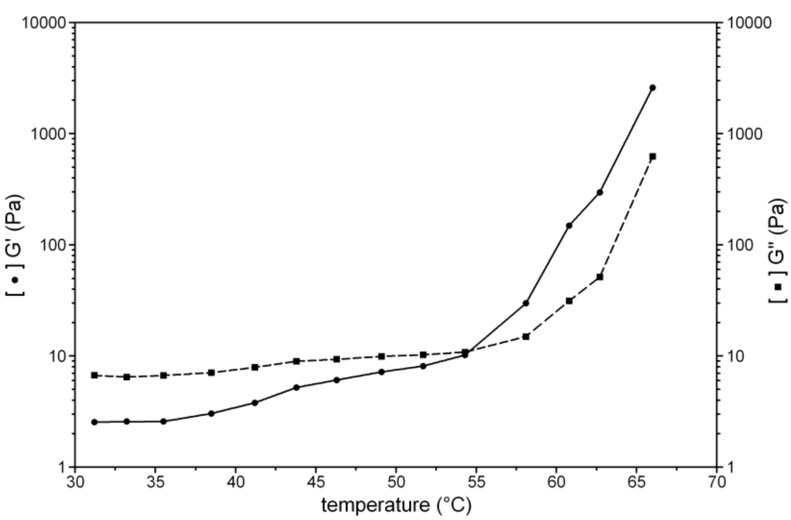
Effect of Molecular Weight



Gellation of Polymer Solution



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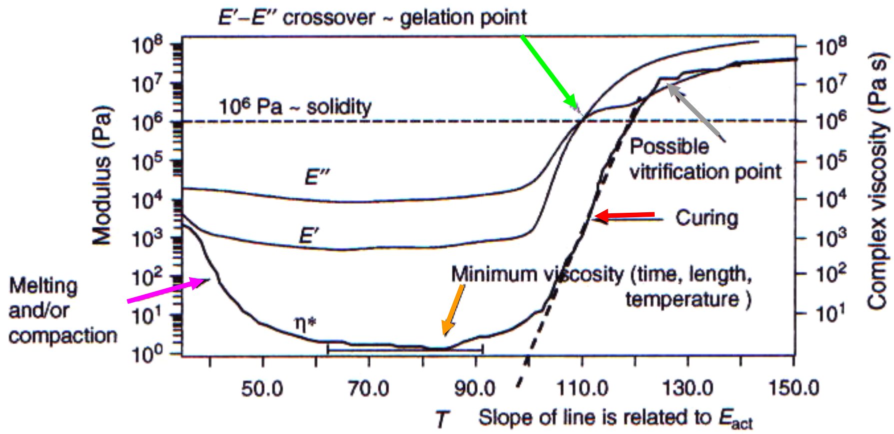
Thermoset Curing



Refer to Slide 87- Part 4

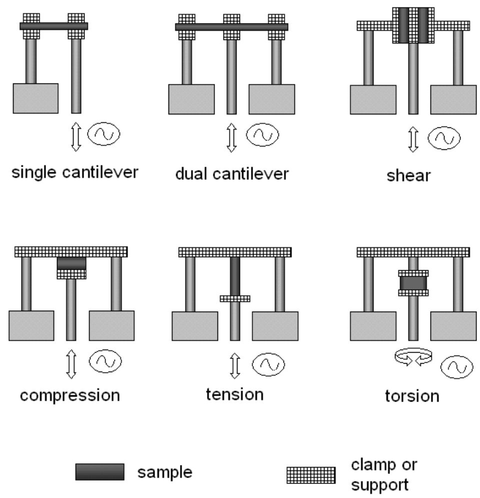
جمع بندی

۱ • فرآیند ساخت نانوکامپوزیت های پلیمری (Processing)

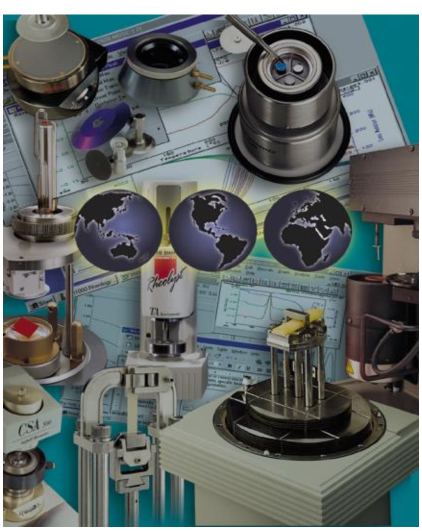
۲ • مشخصه یابی خواص پلیمرها و نانوکامپوزیت ها (Characterization)

۳ • DMA مشخصه یابی مکانیکی/حرارتی کامپوزیت ها

Test Configurations



Thermal Analysis Techniques



- Differential Scanning Calorimeter (DSC)
- Thermo-Gravimetric Analysis (TGA)
- Dynamic Mechanical Analysis (DMA)
- Thermo-Mechanical Analysis (TMA)

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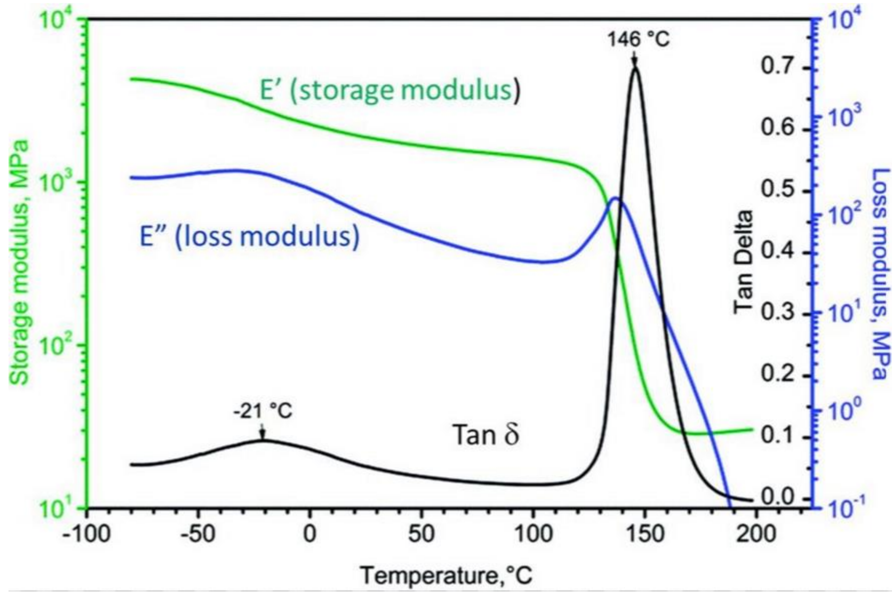
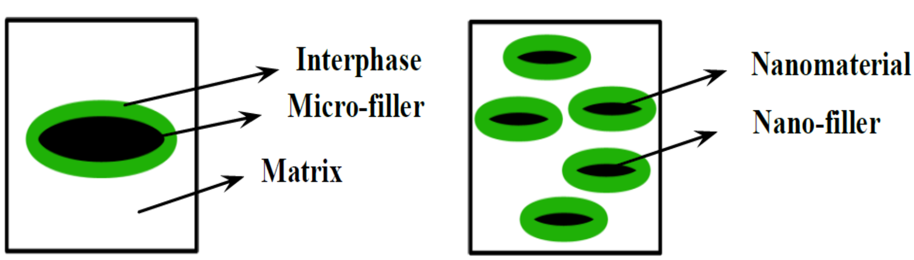
Loss, Storage Modulus and tan δ



Why Micro/Nano-materials?



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